Japan Patent Office
Kokai Patent Publication No. 80764 - 1984, May 10, 1984

Electroless plating bath of platinum or platinum-palladium alloy

Patent Application No. 190587 - 1982
Date of Application : October 28, 1982

Inventor : E. Toriyasu
9-20 3-Chome, Higashi Kuhoji, Yao Shi
Inventor : K. Takenaka
4-13 3-Chome, Satsukigatake, Ikeda Shi
Inventor : Y. Kawami
92 Katazoe Cho, Kawachinagano Shi
Applicant: Director, Industrial Technology Institute
Designated Attorney : Director, Osaka Technology Test Laboratory, Industrial Technology Institute

Specification

Title of Invention: Electroless plating bath of platinum or platinum-palladium alloy

Claims of the Patent

(1) Electroless plating bath of platinum or platinum-palladium alloy which is characterized by that it contains (a) the nitro complex salt or (and) nitro ammine complex salt of platinum, or the nitro complex salt or (and) nitro ammine complex salt of this (these) and palladium, (b) hydroxyl amine salt and (c) hydrazine and that the pH is 10 ~ 18.

Detained Description of the Invention

This invention is related to the hydrazine type plating bath for the electroless plating of platinum or platinum - palladium on the metal or non-metallic surface. In particular, it is related to the novel plating bath which has excellent stability of the bath solution, high utilization ratio of the platinum or platinum - palladium alloy and, also, a low operating temperature.

Regarding the electroless plating of platinum, the known literature is few. Analogizing from the electroless plating methods which are commonly practiced, one can consider the bath solution which consists of the platinum salts and the

reducing agent selected from hydrazine, borohydride salt, alkyl amine boran, hypophosphites, formalin, etc.

However, the reduction of platinum ion proceeds relatively fast compared to the case of other metals and so the stability of the bath solution is poor. For this reason, it is believed that, in any combination of the above described ones, growing the plating layer selectively on the surface of the body being plated would be difficult.

For example, among the reducing agents mentioned above, the borohydride salt has a too strong reducing power and so the reduction of platinum proceeds too much and the platinum separates out in the bath (i.e. self decomposition); therefore, to suppress the reaction, it is necessary to add the stabilizing agent. But, for this case, a suitable stabilizing agent can not be found. Also, the alkyl amine boran type bath solution is definitely stable and there is little self decomposition but the reduction temperature is high and it occurs at 70 ~ 80 deg C. Consequently, the range of usable plastics is narrow ; also, the amount of evaporation of ammonia caused by the high temperature is large and so there is the shortcoming that the process is not preferable in terms of the operational aspects. Next, with regard to the hypo phosphite and formalin, the reducing power is weak and so the reduction needs to be conducted at a high temperature : however, in case of the high temperature, the self decomposition occurs severely and a stabilizing agent which can suppress this self decomposition can not be found. However, in the case of using hydrazine as the reducing agent, although it is impossible to apply the bath solution that was used in the past for the plating of other metals directly to platinum because the stability of the bath solution is very poor, it is believed that, by selecting the form of the platinum ion and the stabilizer, one can improve the stability of the bath solution.

To improve the stability of the hydrazine type bath solution of platinum, the present inventors conducted extensive studies of various platinum ion complex salt and the coexisting stabilizing agent and, as the result, it was found out that, when the platinum is used particularly as its nitro complex salt or nitro ammine complex salt and also when the hydroxyl amine salt is used as the stabilizing agent, the stability of bath solution is improved remarkably and that, in this case, the selective precipitation property is enhanced remarkably and that the platinum utilization ratio is very high at over 95 % and that the plating can be conducted

at a low plating temperature of below 60 deg C and that, as the boride is not contained, the plating layer does not harden and the adhesion strength is high and that, in addition, when the said platinum complex salt and the nitro complex salt or nitro ammine complex salt of palladium are used simultaneously, the platinum - palladium alloy is plated in the same way. Thus, this invention has been accomplished.

Thus, this invention is related to the electroless plating bath of platinum or platinum-palladium alloy which is characterized by that it contains (a) the nitro complex salt or (and) nitro ammine complex salt of platinum, or the nitro complex salt or (and) nitro ammine complex salt of this (these) and palladium, (b) hydroxyl amine salt and (c) hydrazine and that the pH is 10 ~ 18.

As for the platinum nitro complex salt or platinum nitro ammine complex salt, for example, crystal of $K_2[Pt(NO_2)_4]$, $Na_2[Pt(NO_2)_4]$, $(NH_3)_2Pt(NO_2)_2$, etc is used by dissolving in ammonia water ; or, to the solution of ammine complex salt or chloro ammine complex salt of platinum, the salt such as alkali metal salt of nitrous acid is reacted in ammonia water and the product is used. However, the coexisting ion in the bath solution frequently gives influence on the plating condition and, so, considering the quality control aspect of the plating, it is preferred to use the crystal which is as pure as possible. In the case of using the crystals, usually one type is used but it is all right to use 2 types or more.

In the case of plating the platinum - palladium alloy, the crystals of the said platinum complex salt and the palladium nitro complex salt or (and) palladium nitro ammine complex salt are dissolved in ammonia water for use; or, to the solution of ammine complex salt or chloro ammine complex salt of platinum and the ammine complex salt or chloro ammine complex salt of palladium, nitrous acid salt is reacted in ammonia water and the product obtained is used. As for the above mentioned palladium complex salt, examples are the crystals of $K_2[Pd(NO_2)_4]$, $Na_2[Pd(NO_2)_4]$, $(NH_3)_2Pd(NO_2)_2$, etc. In the case of using the crystal, at least one type of these is used. At the time of plating the platinum - palladium alloy, the mol ratio of platinum and palladium as metal is normally about 0.1 ~ 1.5 mols of palladium to 1 mol of platinum.

As for the hydroxyl amine salt which is used in this invention, the water soluble salt such as the hydrochloride,

sulfate, nitrate, etc. are preferred.

As for the hydrazine in this invention, the one which becomes hydrazine in the state of water solution, e.g. the hydrate, hydrochloride, sulfate of hydrazine can be used suitably.

As to the composition of bath solution of this invention, the concentration of platinum or platinum - palladium is 5×10^{-4} ~ 5×10^{-2} M/ liter (in the case of platinum, 0.1 ~ 10 g/ liter), preferably 2.5×10^{-3} ~ 2.5×10^{-2} M/liter (in the case of 0.5 ~ 5 g/liter), the hydroxyl amine is 0.0014 ~ 0.7 M/ liter (in the case of hydrochloride, 0.1 ~ 50 g/ liter), preferably 0.0014 ~ 0.014 M/ liter (in the case of hydrochloride, 0.1 ~ 1 g/ liter) and the hydrazine is 0.003 ~ 1.5 M/ liter (in the case of mono hydrate, 0.15 ~ 75 g/ liter), preferably 0.003 ~ 0.3 M/ liter (in the case of mono hydrate, 0.15 ~ 15 g/ liter). In this invention, the bath solution of the above described composition is prepared to the pH in the range of 10 ~ 13, preferably 11 ~ 12, by ammonia water or alkaline pH buffer solution, before the use.

If the pH is above 13, the rate of reduction is fast and self decomposition occurs easily. Also, if the pH is lower than 10, the rate of reduction is small and the plating time is long. When the hydroxyl amine is less than 0.0015 M/ liter, stability of the bath solution is poor and, also, if it exceeds 0.7 M/ liter, growth of the plating layer is suppressed extremely and so it is not preferable.

To the plating bath of this invention which is prepared as described, the material to be plated which was given the activation treatment in advance is dipped and, at the temperature of in the range of room temperature ~ 60 deg C, preferably 30 ~ 50 deg C, the reduction reaction occurs catalytically and the plating layer of good quality of platinum or platinum - palladium alloy grows. If this plating temperature is lower than the room temperature, plating does not occur easily. Also, if the plating temperature exceeds 60 deg C, the self decomposition starts to occur. Within the said range of temperature, the plating proceeds well and, at this time, the reaction ratio of the platinum or platinum - palladium in the bath solution reaches 95 ~ 98 % and the self composition in the bath solution or the depositing on the reaction vessel wall does not occur at all. The plating time depends on the shape of the material being plated and so it is not constant but, for example, in the case of obtaining the platinum plating layer of about 2 um, it is a

short time of 1.5 ~ 2 hours.

In the plating bath of this invention, the said platinum complex salt itself is very stable (same with the said palladium complex salt also) and, when the hydroxyl amine salt is added, more stable complex is formed and the self decomposition is suppressed almost altogether.

Consequently, in the plating bath of this invention, when the material to be plated is not dipped, the self decomposition does not occur for a long time period and so it has a very good stability.

As for the object material to which the plating bath of this invention can be applied, examples are the industrial materials such as the electronic parts or electrode material, e.g. copper, nickel, iron, and their alloys, and titanium, tantalum. It can be applied also to the synthetic resins such as acrylo nitrile, butadiene - styrene copolymer (ABS) resin, polyamide resin, carbonate resin, and to the common material to which the electroless plating can be applied, e.g. glass, ceramics, etc.

Also, this can be applied in the manufacturing of the unit cell of water electrolysis tank for producing hydrogen or oxygen in which platinum is used by being put into junction to the cation exchange membrane. In the making of this type of junction, the plating bath of this invention is superior to the existing plating bath of the alkyl amine boran type with less contamination of the membrane.

In all cases, it is preferred to conduct a preliminary activation treatment to the material to be plated.

In the case of metal, it is dipped in the water solution of the salt of palladium, platinum, rhodium, etc after its surface is cleaned and, when necessary, it is activated by conducting the dip - reduction treatment in continuation by using the water solution of borohydride salt and, then, it is dipped in the plating bath of this invention.

In the cases of polymeric material, glass, ceramics, also, the surface hydrophilization, sensitizing treatment and activation treatment which are normally used when chemical plating of copper, nickel, etc is conducted on the surface of these materials are conducted and then the dipping is done in the plating bath of this invention.

Also, in the case of ion exchange membrane, the surface roughening and cleaning treatment is conducted and then, depending on the polarity of the membrane, the anionic or cationic platinum complex ion is adsorbed and, in continuation, reduction is done by sodium borohydride solution to place the first layer of about 0.5 ~ 2 um; after this, dipping is done in the plating bath of this invention to let it grow.

The plated layer obtained by using the plating bath of this invention does not contain boron in comparison to the platinum or platinum - palladium alloy which were deposited by using, for example, the borohydride salt, dimethyl amine boran, etc and so it has a low hardness and good flexibility and the junction strength is high. Therefore, this is suitable for the plating of electrode materials. It is also suitable for the plating to the flexible substrate as in the case of the membrane - electrode junction.

In addition to the plating of platinum or platinum - palladium alloy, the plating bath of this invention can be applied also to the plating of the metal alone such as iridium, rhodium, etc that makes stable nitro complex salt or nitro ammine complex salt like platinum or palladium, or the plating of the alloy of this metal with platinum.

In the following, the invention is explained more specifically by giving examples of application.

Example of Application 1

Using the cationic exchange membrane of perfluoro carbon sulfonic acid type [made by DuPont Co., [Naph Ion 117], membrane thickness 7 mils (about 0.175 mm)], platinum was joined to the circular part of a diameter of about 80 mm.

As for the pretreatment of the membrane, first the sand blast roughening was conducted and then the boiling was done in 4N HCl for cleaning and then the washing with hot water was done.

The treated membrane was held in the plating cell and, at the two sides of the membrane, the platinum ammine complex salt solution (platinum 50 mg/ 100 ml) which was obtained by boiling platinum tetra chloride in ammonia water was placed and the dipping was done for 2 hours at room temperature. After the washing with water, the sodium boro hydride 0.05 % solution of pH 12 was added to the same cell and reducing

was done for 2 hours at 40 ~ 60 deg C to let the platinum layer of about 1 um thickness deposit on both surfaces of the membrane.

This activated membrane was dipped in the chemical plating bath of the following composition.

(1) Dinitro diammine platinum	0.5 g
(2) Ammonia water (28 %)	50 ml
(3) Water	250 ml
(4) Hydroxyl amine hydrochloride 50 % water solution	10 ml
(5) Hydrazine mono hydrate (80 % as hydrazine)	5 ml
(6) Water — Total amount	400 ml
(7) pH	11.7

Bath solution was prepared by having (1) (2) (3) heated and dissolved and then adding (4) (5) (6).

Plating was conducted at 40 ~ 50 deg C for 2 hours and the amount of platinum that deposited out was 3 mg/ cm2 and the plating thickness was about 3 um.

During this period, separation out did not occur in the bath solution and the utilization ratio of the platinum in the original solution was about 98 %.

Example of Application 2

Using the composite membrane of the sulfonic acid type and carboxylic acid type (made by DuPont Co., [Naph Ion 901]), platinum was joined to the side of carboxylic acid membrane.

In the same way as in Example of Application 1, the membrane was held in the cell and dipping was done in the platinum ammine complex salt solution and, after this, reducing was done with the sodium borohydride of pH 23 to prepare the first reduction layer and, after this, dipping in the chemical plating bath of the following composition was done.

(1) Potassium tetra nitro platinate	0.6 g
(2) Ammonia water (28 %)	20 ml
(3) Water	100 ml
(4) Hydroxyl amine hydrochloride	0.2 g

(5) Hydrazine mono hydrate (80 % as hydrazine)		8 ml
(6) Water	Total	200 ml
(7) pH		11.8

The bath solution was prepared by having (1) (2) (3) heated and dissolved to obtain the water solution and then adding (4) (5) (6).

During this period, separation out did not occur in the bath solution and the utilization ratio of platinum in the original solution was 98 %.

Example of Application 3

The copper plate sample (2 x 4 cm) was given a degreasing and cleaning treatment by using sodium cyanide solution and then dipping was done in the 5 % palladium chloride 2N - hydrochloric acid solution for 30 seconds at the room temperature for activation. After washing with water, dipping was done in the following plating bath solution (prepared in the same manner as in Example of Application 2) at 40 deg C for 2 hours to obtain the platinum - palladium alloy plating of about 2 um.

No decomposition occurred in the bath solution and the utilization ratio of metal was 96 % in all cases.

(1) Potassium tetra nitro platinate		0.05 g
(2) Potassium tetra nitro palladiumate		0.05 g
(3) Ammonia water		5 ml
(4) Water		30 ml
(5) Hydroxyl amine hydrochloride		0.1 g
(6) Hydrazine mono hydrate (80 % as hydrazine)		1.5 ml
(7) Water	Total	40 ml
(8) pH		11.8

Example of Application 4

Nickel test piece (2 x 4 cm) was degreased with alkali and this was dipped for 80 seconds in the solution of rhodium chloride 2 g, hydrochloric acid 10 ml, water 100 ml for activation. After this, it was washed with water and, by using the bath solution of the following composition, the plating treatment was conducted at 40 ~ 50 deg C for 2 hours.

(1)	Dinitro diammine platinum	0.08 g
(2)	Ammonia water (28 %)	5 ml
(3)	Water	20 ml
(4)	Hydroxyl amine hydrochloride	0.1 g
(5)	Hydrazine mono hydrate (80 % as hydrazine)	1.5 ml
(6)	Water	40 ml
(7)	pH	11.5

On the surface of nickel, platinum plated layer of about 2 um thickness was obtained and the utilization ratio of platinum was 98 %.

Example of Application 5

To a plate-shaped sample (3 x 4 cm) of 2 mm thickness made of ABS resin (made by Nippon Gosei Gomu (K.K.)), the platinum plating was conducted.

As for the pretreatment of the sample, the activation was applied by the known chromic acid etching and the catalyst bath and activation bath.

As for the platinum plating bath, the one having the composition of Example of Application 1 was used. Dipping was done at 40 ~ 50 deg C for 2 hours to obtain the plating of about 2 um. During this period, decomposition of the bath solution was not observed and the utilization ratio was 97 %.